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THE ESTIMATION OF MINUTE AMOUNTS OF ARSENIC IN FOODS.

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INTRODUCTION.

The poisonous character of arsenic compounds and their wide natural distribution make the accurate determination of arsenic in foods and drinks a subject of great importance to food chemists. Particularly is this true in relation to the enforcement of the Food and Drugs Act enacted by Congress. A regulation prescribing a limitation of arsenic allowable in food products must necessarily be drawn to protect consumers, including children and the debilitated, from all possible harmful effects. The small amount of material available in some cases, as, for instance, when it is necessary to determine the arsenic contained in the coating of chocolate candies, necessitates an extremely delicate test. It can be readily appreciated how sensitive and delicate the method must be which will detect and estimate accurately 0.0001 per cent of arsenic contained in a gram of organic matter. To complicate any method employed there is the possibility of the glass apparatus and the reagents used containing arsenic in appreciable amounts. This is especially true of hydrochloric acid and lead glass; therefore all reagents and apparatus must be tested to insure their absolute freedom from arsenic. The oxidation of the organic material, the generation or liberation of arsin, the deposition of the arsenic mirror or stain, the capacity of the apparatus, the neutrality of the calcium chlorid, the exclusion of air or oxygen, the perfect drying of the gas, and even the time of operation and the rapidity of hydrogen evolution not only must be carried out always alike, but experiment must determine the exact conditions necessary. An experience of nearly a year in this line of work has shown so clearly that success depends largely on following certain slight precautions which might at first be thought of minor importance that a description of the apparatus and the method followed may prove of interest to others. The method employed by the authors is a modification of the well-known Marsh-Berzelius method.

Since Marsh described this test[1] and Berzelius improved upon it many analysts have suggested modifications and improvements which have increased materially the delicacy of the method. Practical methods embodying these changes have been described by Lockemann[2] and Bishop.[3]

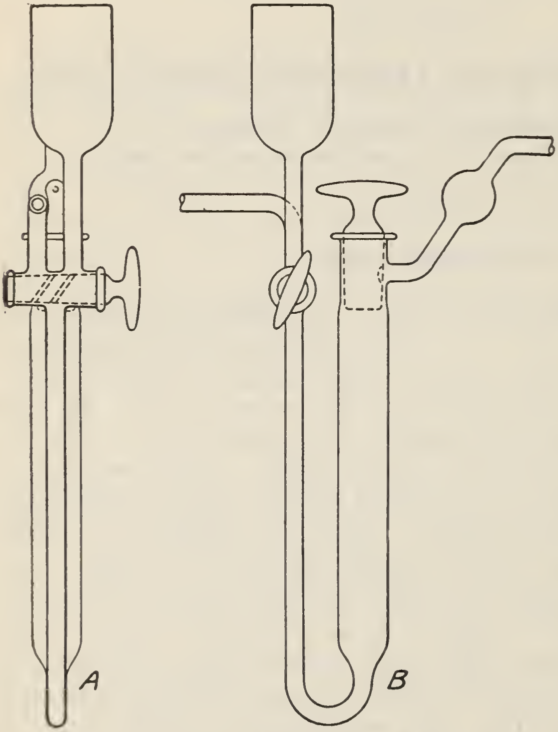

Fig. 1.—Generator: *A*, end view; *B*, side view.

APPARATUS FOR THE DETERMINATION OF ARSENIC.

The form of apparatus used by Bishop for the determination of arsenic in sulphuric acid is mainly the one adopted by the authors and it has proved sensitive, accurate, and reliable when the precautions described later are diligently followed. This apparatus consists essentially of three parts—the generator, drying tube, and deposition tube.

The generator is a one-piece glass apparatus readily made by a glass blower. The one here employed was improvised from a funnel tube, a three-way stopcock, and half of a glass-stoppered U tube (see fig. 1). The capacity of the zinc chamber is less than 10 cc. Its size can be increased by having it in the form of a bulb at a slight loss in the delicacy of the test.

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[1] New Edin. Phil. J., 1836, p. 229.

[2] Zts. angew. Chem., 1905, *18*: 416.

[3] J. Amer. Chem. Soc., 1906, *28*: 178.

The drying tube is filled with sifted calcium chlorid, which should be tested to insure its neutrality. Much of the calcium chlorid obtainable is alkaline and will retain traces of arsenic in the test. Bishop gives directions for preparing a suitable reagent in such cases. In the end of the calcium chlorid tube nearest the generator is placed some dried lead acetate cotton (made from absorbent cotton soaked in 1 per cent lead acetate solution).

The deposition tube is made from hard combustion tubing 7 mm external diameter, drawn to a capillary and cut so that it has a total length of about 20 centimeters, of which 10 centimeters is the length of the tube to the flame and 5 is the tapering distance to the mirror. The diameter of the capillary where the mirror is to be deposited, once established, must be kept uniform in all tests by means of a gauge. An external diameter of No. 8 standard wire gauge (0.128 inch) is well suited to the purpose, although it is probable that a smaller bore would be better adapted to detect and estimate smaller amounts of arsenic than 1 micromilligram. The tube is cooled at this point by a small moist cotton string wound two or three times around it and kept wet by a slow stream of water from above. The deposition tube is heated by a Tirrill or Chaddock burner, the flame being protected from air drafts by a brass gauze chimney about 1¼ inches in diameter. The tube is protected and evenly heated by a cylinder of brass gauze which passes horizontally through the gauze chimney. Asbestos guards through which the tube runs are suspended at each side of the chimney.

The generator is rigidly clamped into position at the proper height to allow it to be partly immersed in a beaker of cold water which stands on an electric stove. The complete apparatus is shown in figure 2.

METHOD FOR THE DETERMINATION OF ARSENIC.

REAGENTS.

The zinc should be free from arsenic and at the same time give a brisk evolution of gas with dilute acid. It should be "feathered" or cut into small pieces, thoroughly washed with water and then with a little pure dilute hydrochloric acid, and rinsed before being used in the generator. The sulphuric acid and nitric acid are the pure concentrated acids, which can readily be obtained arsenic free.

PREPARATION OF THE SAMPLE.

The preparation of the sample is the first important step, and there are many chances for error both to lose and to acquire arsenic in this operation. Wet digestion of the organic material was tried and found satisfactory. A sufficient amount of the uniformly mixed sample is taken to produce a mirror preferably of 3 to 5 micromilligrams of metallic arsenic or As_2O_3 as the analyst selects for his standards. One gram of sample will contain as many parts of arsenic per million as there are micromilligrams of mirror. If 1 gram of sample produces a 1 micromilligram mirror, that substance contains 1 part of arsenic in 1,000,000.

The sample is introduced into a 100 cc Jena glass long-necked Kjeldahl digestion flask, from 1 to 2 cc of arsenic-free concentrated sulphuric acid are introduced, and 5 cc or less of arsenic-free concentrated nitric acid added. After the first violent action is over the flask is held in an inclined position over a low naked flame with continual agitation until the organic material begins to char, when a few drops of nitric acid are introduced into the boiling acid. This addition of nitric acid is repeated as often as necessary to oxidize and render the solution colorless. The entire process usually takes 15 to 30 minutes on a 1 to 5 gram sample. When oxidation is complete allow the flask to cool and transfer the digestate with distilled water to a small porcelain casserole, add 5 cc of a saturated sulphurous acid solution, evaporate excess of water, and free the solution from sulphurous acid on a water bath. Dilute the sulphuric acid residue with three volumes of water. Cool and introduce into the

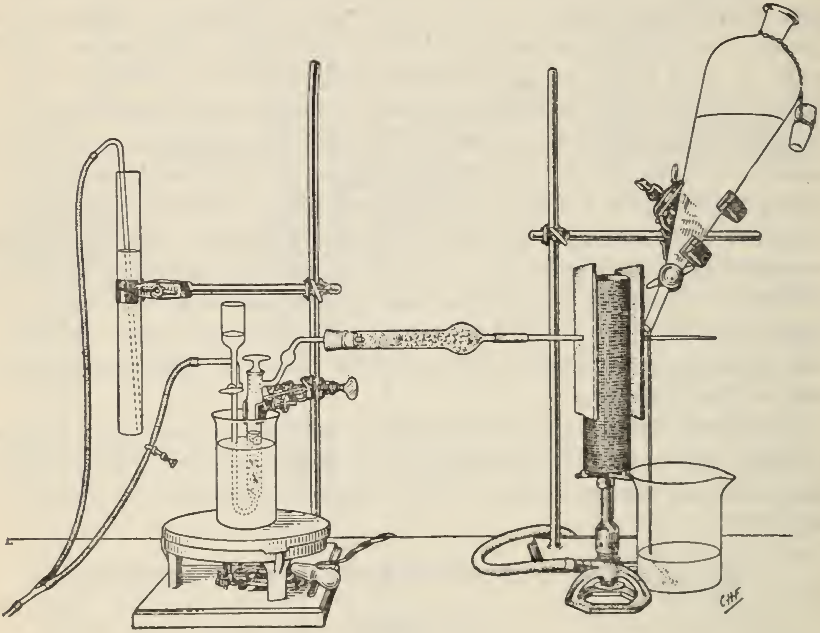

Fig. 2.—Complete apparatus for the determination of arsenic.

funnel tube of the apparatus. Rinse the casserole with a small quantity of dilute sulphuric acid (1 to 3) and reserve the rinsings to rinse funnel when the original solution has been allowed to run into the generator, which has been previously half filled with arsenic-free zinc and 4 drops of amyl alcohol added.

EVOLUTION OF THE ARSIN.

By means of the side tube and the proper adjustment of the three-way cock pass a moderate stream of carbon dioxid (conveniently from a cylinder of the compressed gas) through the entire apparatus until the air is expelled, which usually requires only a minute or two. The current of carbon dioxid may be regulated by a by-pass and a column of water, as shown in the illustration. The cooling string and the water drip are now properly adjusted, the burner lighted, and the flame moved to a position so that the section of the tube where the cooling string is and where the mirror will be deposited is not over 5 mm from the chimney. The current of carbon dioxid is now shut off by the three-way cock and the solution, not more than 4 or 5 cc in volume, is introduced into the zinc chamber through the funnel tube, care being taken not to introduce air. If vigorous action begins upon introduction of the solution add the solutions and rinsings gradually, forcing the last portions over with a stream of carbon dioxid if necessary. The zinc chamber should not be more than five-sixths filled when containing all the sample. When vigorous action has ceased or the evolution of gas is not sufficiently rapid, use the stove to warm gradually the water in the beaker and hasten action. At the end of half to three-quarters of an hour remove the beaker and stove and again pass a slow stream of carbon dioxid to sweep out remaining traces of arsin. All the arsenic should now be deposited in a metallic brown stain from 1 to 3 mm long, which may be easily compared with standard stains.

PREPARATION OF STANDARD MIRRORS.

Standard tubes of 1, 2, 4, 5, 7.5, and 10 micromilligrams of arsenic are made in the same way as above from a solution of arsenic prepared as described in Bishop's article. The strong stock arsenic solution should be prepared and kept for use when required. The dilutions for making the standard tubes are made with boiled distilled water each day as needed. After a satisfactory mirror is obtained the tube is sealed in the flame at the small end, some phosphoric anhydrid introduced after protecting the mirror by a small plug of cotton, and the open end sealed with sealing wax. Standard tubes should be kept in the dark and, thus protected, will keep for reasonable lengths of time. Comparison of the mirrors is best made by diffused daylight. A simple form of camera, as recommended by Sanger,[1] works well. The figure of the standard mirrors, drawn from a photograph (fig. 3), shows fairly well the considerable differences in intensity between adjacent standards. These wide differences contribute much to the delicacy of the test. The 1-micromilligram mirror is a characteristic stain easily seen. As a matter of fact a 0.5-micromilligram mirror is distinctly perceptible even in the comparatively large tube adopted for the authors' standard.

PRECAUTIONS.

Arsenic-free reagents, apparatus, and reagent bottles must be used. Jena or other glass vessels found to be free from arsenic should be used for the wet digestion and to contain the acids.

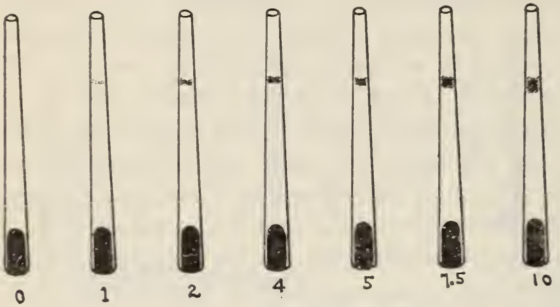

FIG. 3.—Standard mirrors.

A determination should be completed the same day as begun, taking no risks of collecting arsenic from dust or of losing it by volatilization.

Digestion with sulphuric acid and nitric acid must not be allowed to proceed beyond incipient charring without the introduction of more nitric acid. Small amounts of arsenic acid may otherwise be reduced and volatilized.

To obtain the best results the use of sulphurous acid has been found advisable, following the sulphuric-nitric acid digestion, for the purpose of uniformly reducing all arsenic compounds to the arsenious form.

The quantity of acid introduced and the temperature of the generation of gas play an important part in the production of a good arsenic mirror. In the authors' opinion, the most satisfactory mirrors were obtained when the sulphuric-acid solution of the sample was introduced in small portions at a time, followed by the rinsings of 1 to 3 acid, the whole being kept moderately cool until all the sample was in the zinc chamber and the evolution of gas had slowed up, finally gradually heating in the water bath to incipient boiling.

The drying tube must be frequently charged with freshly prepared neutral calcium chlorid and dry lead acetate cotton. No trace of moisture or air must be allowed to enter the arsenic tube during deposition. Failure to observe this precaution will reduce the delicacy of the test and give grayish or otherwise imperfect mirrors.

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[1] Amer. Chem. J., 1891, *13:* 439.

Amyl alcohol or some similar volatile organic material, as recommended by Thomson,[1] is necessary for the production and even distribution of a satisfactory brown mirror. Four drops of amyl alcohol in the zinc chamber were found adequate.

Antimony, if present, will produce an interfering mirror and must be proved absent or else separated by the well-known tests and methods.

The presence of iron affects the results, and according to Harkins[2] must be overcome by the use of heat or the addition of arsenic-free stannous chlorid. Heating the generator has been found preferable in that it avoids the use of another reagent.

For making standard mirrors prepare dilute arsenic solutions with boiled distilled water from the 1 per cent arsenic standard stock solution each day needed. Do not use dilutions when more than a few hours old. In preparing the standard mirrors, as well as in the actual determination of arsenic, it is essential for conclusive results that two, or better three, concordant mirrors should be obtained in each case.

Use rubber connections, where unavoidable, which have been previously treated with boiling dilute caustic soda to remove sulphur compounds.

Approved:
JAMES WILSON,
Secretary of Agriculture.
WASHINGTON, D. C., *April 11, 1912.*

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[1] Chem. News, 1901, *84:* 173.

[2] J. Amer. Chem. Soc., 1910, *32:* 518.

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